

mechanical or chemical conditions, a few typical cases have been selected.

Figure 5 shows a welded bubble tower for a Holmes Manley cracking unit, 6 feet 6 inches in diameter and 46 feet long, with a 2.25-inch shell and 2.5-inch head thickness. The operating conditions are 350 pounds per square inch pressure at 900° F. The metal is low-carbon steel of 60,000 to 70,000 pounds per square inch tensile strength.

Of particular interest, owing to its high working pressure of 1400 pounds per square inch, is the unit shown in Figure 6. The metal is a special, high-strength steel (70,000 to 80,000 pounds per square inch) of a higher carbon and manganese content than is usually used in boiler plate. The shell is 4.125 inches thick. This was the first welded boiler drum of so large a size to be constructed for such high working pressure. Previously, similar parts were made by forging. The use of fusion welding for work of this kind is far more economical.

One of twenty-four special units to be used in the production of a new process lubricating oil is shown in Figure 7.

An interesting story is that of the tank in Figure 8. It became necessary to replace a riveted stainless steel unit by a larger welded one. This was accomplished by cutting out the riveted joints, inserting a middle section, and welding. Thus the requirements were met with the loss of a relatively small amount of valuable stock.

The tanks in Figure 9 are of stainless steel, built to fulfill the requirements for units of high chemical resistance to

operate under vacuum. Contamination of the product by metal or the leakage of traces of air into the tank contents would be destructive.

An interesting installation involves five welded butane tanks, of 15,000 gallons capacity each, 8 feet in diameter, 47 feet high, and operating under a working pressure of 150 pounds per square inch for the San Diego Consolidated Gas & Electric Company. Two of these are shown in Figure 10.

The shop photograph in Figure 11 includes fifteen welded pressure vessels for a vapor recovery system built for an Argentine Government gasoline plant. In the background may be seen the large annealing furnace with rolling arch cover partly in place and two of eight welded high-pressure boiler drums being made for the city of Wyandotte, Mich.

ACKNOWLEDGMENT

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Zinc Oxide-Chromium Oxide Catalysts for Methanol Synthesis

M. C. MOLSTAD AND BARNETT F. DODGE, Yale University, New Haven, Conn.

DURING the entire period of the development of the synthetic methanol process zinc and chromium oxides were known to be important constituents of active catalysts, and were mentioned in the basic patent (3) granted in 1913. A considerable number of more recent patents have specified zinc oxide alone or mixtures of zinc oxide and chromium oxide in various proportions. Patart (20) in 1926 reported that the best alcohol catalysts known to him consisted of such mixtures because they give very satisfactory practical yields, are easy to prepare, are persistent in activity, have great insensitiveness to poisons, and are easily regenerated. More recently, Bone (4) has stated that the best methanol catalyst seems to be $3\text{ZnO} \cdot \text{Cr}_2\text{O}_3$, to which has been added a fractional percentage of copper nitrate. Catalysts of the zinc oxide-chromium oxide type have therefore been prepared and tested in the course of a broad research program on methanol synthesis carried out in this laboratory.

The present paper reports methanol synthesis tests on zinc oxide, chromium oxide, and six different mixtures thereof, and is the first contribution to the literature in which the entire range of catalyst composition has been systematically studied at a series of temperatures. These tests served to confirm the first three of the characteristics listed by

Zinc oxide, chromium oxide, and a series of mixtures of these have been tested for methanol synthesis activity over a wide temperature range at a pressure of about 180 atmospheres. Results are given on (1) the effect of temperature, space velocity, and methods of preparation upon the catalyst activity and the purity of the methanol, (2) the stability of the catalysts during extended operation, and (3) their resistance to overheating. Some observations on volume shrinkage of catalysts and the variation of temperature throughout a small column of catalyst are also included.

Patart; but it is particularly desired in this paper to bring out two features of this type of catalyst that have not been stressed in any previously published work.

The first of these features involves the marked degree to which chromium prevents the loss of activity suffered by catalysts of high zinc content when exposed to temperatures somewhat above the optimum operating temperature. The catalysts in which the molecular ratio of zinc to chromium was about 1 have, in fact, shown continuous improvement during an extended period of use above the temperature of maximum activity. Such observations have not been previously reported, and it has been generally held that exposure of catalysts to temperatures higher than normal operating temperature should be strictly avoided (1). The only exceptions which have come to the notice of the writers

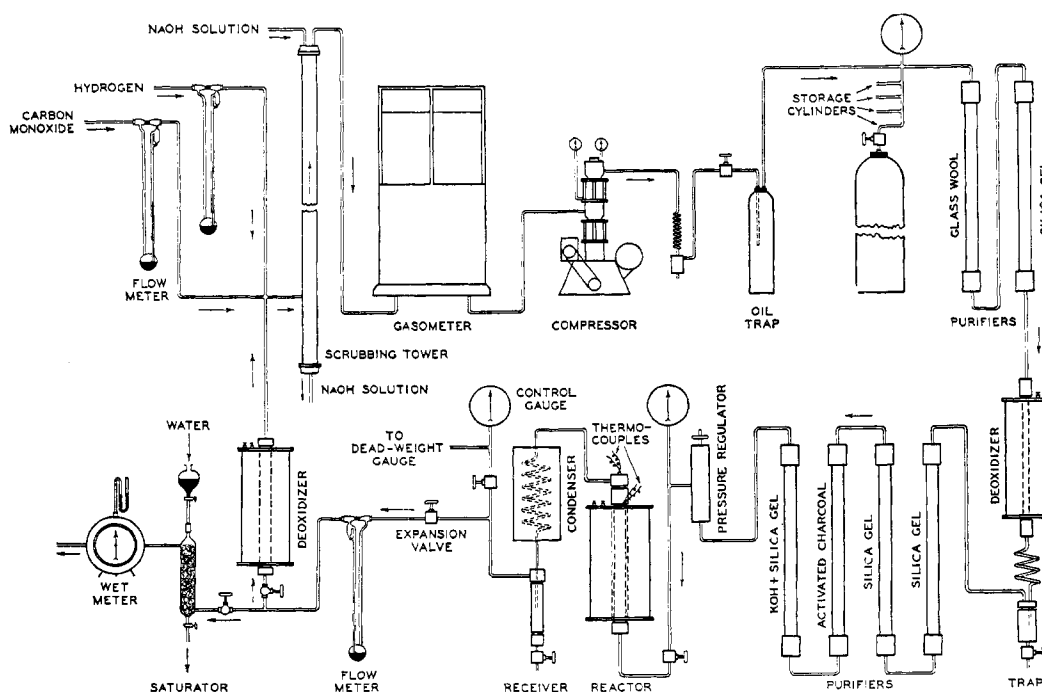


FIGURE 1. DIAGRAM OF APPARATUS FOR TESTING METHANOL SYNTHESIS CATALYSTS

are the patents by Lazier (14), in which catalysts made by ignition at 650° to 1000° C. are said to be unaffected by use at high temperatures.

The second feature involves the observation that the catalysts containing approximately equal moles of zinc and chromium are the most active of the series. It has been generally held by previous investigators that the most active catalysts were those containing zinc in considerable excess. Many patents (27) have emphasized this point, specifying atomic ratios of zinc to chromium up to 12 or more. Frolich (9) states that "probably the most interesting fact in regard to the composition of methanol catalysts is the necessity of having the more basic oxide in excess. This point is repeatedly emphasized in the patent literature. . . . Although good catalysts for hydrogenation, the mixtures deficient in the more basic oxide apparently do not produce methyl alcohol from carbon monoxide." Only recently have patents by Lazier (14) and by Lusby (16) specified catalysts having ratios smaller than one. Plotnikov and Ivanov (23) have found this ratio to be about 4 for the most active of their zinc oxide-chromium oxide catalysts. Tests of equal weights of catalysts by Cryder and Frolich (8) gave an optimum ratio of about 3, while their conversion of the data to the usual basis of equal volumes of catalyst indicated an optimum ratio of about 1.5. Evidence of the activity of catalysts of high chromium content was given by Brown and Galloway (5) who found that the catalyst with an atomic ratio of zinc to chromium of 1 had 30 per cent greater activity than the one having a ratio of 2. Natta (18), on the other hand, reports that a catalyst having a ratio of slightly less than 1 was greatly inferior to one in which the ratio was 2.5. There has been great variety in the methods of catalyst preparation and testing employed in the investigations mentioned, which may conceivably account for the apparent disagreement. The present paper attempts to add to the evidence needed to explain the contradictory results obtained in this field.

In addition to the previously mentioned investigators, Audibert and Raineau (2) tested a large number of catalysts, including zinc oxide and chromium oxide. Zinc oxide,

basic zinc chromate, and normal zinc chromate were studied by Morgan, Taylor, and Hedley (17), and by Brown and Galloway (6). Storch (26) tested several zinc oxides, two chromium oxides, and a basic zinc chromate, while Frolich and co-workers (10) tested a zinc oxide in their study of zinc-copper mixtures. Plotnikov and co-workers (23, 24, 25) and Natta and Casazza (18, 19) have tested zinc oxide, chromium oxide, and several mixtures of these, and Lazier and Vaughn (15) have reported results with several pure chromium oxide catalysts. Despite the variety in the methods of catalyst preparation and testing used in the work mentioned, there are a number of cases that are quite comparable and these are treated later in the discussion of results.

EXPERIMENTAL PROCEDURE

CATALYSTS. The series of catalysts studied was prepared by precipitation of the hydroxides upon addition of ammonium hydroxide to a solution of zinc nitrate, chromium nitrate, or mixtures of these compounds at 85° C. Details of the methods of preparation and analysis are given in a paper by Huffman and Dodge (12) covering the methanol decomposition activity of the same series of catalysts.

APPARATUS. A diagram of the arrangement of apparatus used is shown in Figure 1:

Carbon monoxide, made by dehydrating formic acid with phosphoric acid, was mixed with commercial electrolytic hydrogen and with carbon-dioxide-free unconverted gas remaining from the methanol synthesis tests, the resulting mixture being compressed to about 200 atmospheres and stored. The composition of this gas varied only slightly, the average of periodic analyses (in per cent) being 64.5 hydrogen, 31.8 carbon monoxide, 1.7 nitrogen, 1.4 methane, 0.3 oxygen, 0.2 carbon dioxide, and 0.1 unsaturated hydrocarbons. Gas withdrawn from the storage system was purified as shown and passed through a constant-pressure regulator that was checked daily against a sensitive piston gage. The gas then entered a copper-lined reactor, shown in Figure 2, in which a sample of 8 to 12 mesh catalyst having an initial volume of 10 cc. was held in a central position between copper shot, used to preheat the inlet gas, and granular quartz. The annular space occupied by the catalyst had inside and outside diameters of 0.635 and 1.61 cm., respectively, and a length of 5.85 cm.

The recorded temperature of the catalyst was arbitrarily taken as that at the center of the catalyst space as measured in a heavily copper-plated thermocouple well. This temperature is at best only one point in a gradient which is unavoidable owing to the considerable evolution of heat during the reaction.

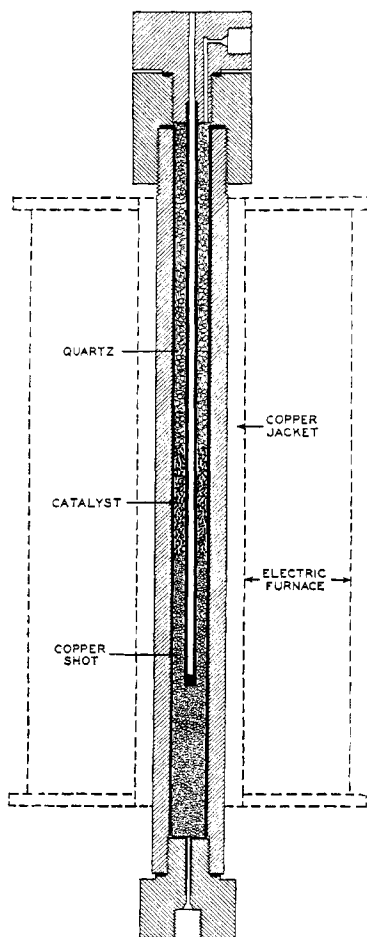


FIGURE 2. METHANOL SYNTHESIS REACTOR

in the catalyst and was practically independent of temperature. The outside temperature was about 20° C. higher than that inside when no reaction was taking place and about 20° C. lower at the maximum observed conversion of 16 per cent of the entering carbon monoxide to methanol. While these figures will be different for the tests of other investigators, they do nevertheless indicate the possibility of an error well worth avoiding.

The liquid products were condensed at 0° C. at the testing pressure and separated from the gas by a trap. The remaining gas was expanded to atmospheric pressure, measured, and returned

to the high-pressure storage system, as described previously. The liquid products were periodically expanded to atmospheric pressure and measured, and the density was determined and in most cases subjected to analysis by distillation. For the larger samples the glass-ring-packed column of Peters and Baker (21) was used, while the unpacked column of Cooper and Fasce (7) was used for smaller volumes. Temperature and volume corrections based on standardization runs were applied to all distillation data. There was moderately good agreement between the percentage of methanol according to the specific gravity and that determined by distillation. In general, when the percentage conversion of carbon monoxide was high, the liquid produced was nearly pure methanol and the correlation between the specific gravity and distillation methods was good, whereas, when the liquid was less than 90 per cent methanol, owing to a low catalyst activity or a high reaction temperature which favored side reactions, the correlation was only fair. In calculating the conversion figures, it has been assumed that the specific gravity of the product is a sufficiently accurate indication of its methanol content.

PROCEDURE. A standard procedure for the preliminary treatment of the catalyst was adopted:

The gas mixture used in testing was passed through the catalyst at 1 atmosphere pressure at a rate of about 30 liters per hour for 6 hours. During the first hour the catalyst temperature, as measured inside the reaction chamber, was raised steadily to 200° C. and then held at this point for 2 hours. During the fourth hour the temperature was raised steadily to 300° C. and maintained at this temperature for the remaining 2 hours. The gas pressure was then increased to the testing pressure of 178 atmospheres absolute (2600 pounds per square inch gage) and the flow controlled at the outlet of the reaction chamber so that an inlet space velocity very close to 25,000 was maintained. This space velocity was calculated on the basis of the volume of catalyst as charged by adding to the volume of unconverted gas the volume of gas converted into liquid products. Measurement of the specific gravity and volume of product during the first hour of any constant temperature run usually made it possible to secure a space velocity between 24,500 and 25,500.

The standard testing procedure began at 300° C. When a substantially constant conversion of entering carbon monoxide to methanol was obtained, the testing of the same sample of catalyst was continued at 25° intervals to 425° or 450° C. While this procedure did not exactly locate the temperature of maximum activity, this point could then be found graphically with sufficient accuracy. A final run was always made at the temperature at which the maximum yield had been previously obtained. Comparison of the results of the two tests at this temperature provided information as to the effect of operation at the higher temperatures on catalyst activity. Following this standard testing procedure, many of the catalysts were further tested to bring out the maximum activity of which the catalyst was capable.

It was not possible to fix a definite length of time for the constant-temperature runs because of unavoidable variations in temperature and gas flow. In general, each run required 3 to 7 hours, the first hour being devoted to obtaining steady testing conditions. At 1-hour intervals the liquid product was removed from the condensate trap and measured. The test at any particular temperature was continued until a satisfactory average value of the condensate volume per unit of time could be obtained. When necessary, the test was extended to detect any trend in the results which might indicate marked improvement or deterioration of the catalyst during the testing period.

TABLE I. EFFECT OF EXTENDED TESTS ON CATALYST ACTIVITY

COM- POSITION	TEMP. ° C.	PER CENT Initial	CONVERSION Final	INTERVENING TESTING, HOURS AT:								
				300° C.	325° C.	350° C.	375° C.	400° C.	425° C.	450° C.	475° C.	500° C.
Pure ZnO	400	6.0	4.0	..	..	..	..	3	2	3	..	..
Zn ₉₂ Cr ₈	350	4.8	3.9	..	..	8	6	6	4	5	..	..
Zn ₉₀ Cr ₁₀	350	9.4	7.5	..	..	..	11	3	2	..	..	..
	375	11.5	10.6	..	..	..	..	3	2	..	..	..
Zn ₇₅ Cr ₂₅	375	14.0	13.7	..	..	..	..	5	2	..	..	..
Zn ₅₅ Cr ₄₅	350	10.8	16.2	8	15	18	8	10	7	..	..	..
	375	12.6	14.4	8	12	15	2	8	2	..	..	..
Zn ₃₀ Cr ₇₀	300	0.2	4.0	6	6	11	11	12	2	..	..	..
	325	3.3	10.2	11	..	11	11	12	2	..	..	..
	350	7.6	13.0	11	3	20	10	16	4	..	..	..
	375	8.6	12.6	11	3	10	8	16	2	..	..	..
	400	8.2	10.4	11	3	10	10	9	2	..	..	..
	425	6.3	7.1	11	3	10	10	9	..	..	..	..
Zn ₉₂ Cr ₈	450	1.8	2.5	..	..	..	..	..	2	..	4	3
Pure Cr ₂ O ₃	400	6.5	6.8	..	..	..	..	..	2	..	..	..

DISCUSSION OF RESULTS

REPRODUCIBILITY. A consideration of reproducibility is of first importance in evaluating any testing procedure. It was not feasible in this work to make the tests continuous, and at the end of each day the catalyst was returned to atmospheric temperature and pressure. It was found, however, that in all the cases in which a constant-temperature run was interrupted by such a shut down or by a run at a lower temperature, or both, the two parts of the run agreed within 2 per cent. In one case a check on the whole procedure of catalyst preparation and testing was made with a pure zinc oxide catalyst, and the results differed less than 5 per cent. Tests of the distillation analyses indicated an accuracy of 1 per cent with the smaller column and about 0.2 per cent with the larger column. In general, it is probable that the total error in the conversion results was in all cases less than 10 per cent, and less than 5 per cent for the higher conversions.

EXTENDED TESTS. A summary of the percentage conversions of inlet carbon monoxide to methanol for all catalysts of the series at all test temperatures during the initial testing procedure is given in Figure 3. It was found that the catalyst consisting of 25 atomic per cent chromium and 75 atomic per cent zinc, both metals initially in the form of oxides, was the most active of the series. This observation is in good agreement with the results of other investigators, as mentioned earlier in this paper. Continued testing, however, disclosed that the members of the series were affected very differently by high-temperature operation. The results of this further testing are shown in Table I and Figure 4, which compare certain initial conversions with the conversions obtained after intervening testing periods at the indicated temperatures. Figure 4 shows the initial and final conversions by the catalyst of the composition $\text{Zn}_{75}\text{Cr}_{25}$ which was given the most complete test of the series. To determine whether further improvement was still possible, this catalyst was held at 425°C . and 1 atmosphere pressure with a small flow of the testing gas for 10 hours. This increased the conversion from 13.0 to 14.7 per cent. A similar treatment at 450°C . for 12 hours gave a slight further increase to 15.3 per cent, which was taken as about the maximum obtainable with this catalyst. Table I shows that catalysts containing less than 25 atomic per cent chromium suffered a decrease in activity during use while those containing more than 25 atomic per cent chromium improved. This effect, which would not be observed in the usual brief test, indicated that the most active catalyst of this type has an atomic ratio of zinc to chromium of around 1 instead of about 3, as found in the early part of these tests and as observed by other investigators. This observation serves to confirm the results of Brown and Gallo-way and of Cryder and Frolich, as mentioned above, the agreement with the latter probably being somewhat fortuitous, considering the uncertainties involved in converting their data from a basis of equal catalyst weights to one of equal catalyst volumes.

EFFECT OF SHRINKAGE. The superior activity of the catalysts with an atomic ratio of zinc to chromium near 1 is in reality not completely disclosed in the present tests.

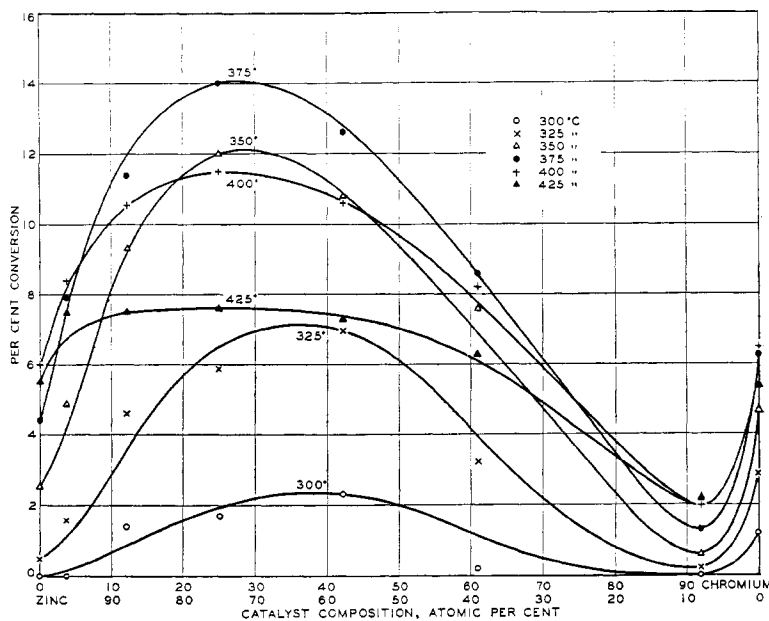


FIGURE 3. PERCENTAGE CONVERSION OF ENTERING CARBON MONOXIDE TO METHANOL DURING STANDARD TESTING PROCEDURE AT 178 ATMOSPHERES

This is ascribed to the fact that the 10-cc. samples of catalysts, charged into the reactor in an unreduced condition, were found after testing to have undergone shrinkage which increased with increasing chromium content; one of the more active catalysts, $\text{Zn}_{55}\text{Cr}_{45}$, had a volume of 4.7 cc. when discharged, and the pure chromium oxide had a volume of 4.0 as compared with 9.9 cc. for the pure zinc oxide. The results obtained near the end of the tests on high-chromium catalysts were thus at actual space velocities more than double the 25,000 recorded above. This unfortunate feature of this series of tests was due to the fact that the catalysts were being reduced *in situ*, since every effort was being made to avoid the possibly injurious oxidation of the reduced catalyst during charging. The tests began with the zinc end of the series; and, since the shrinkage of these was slight and there was nothing in the literature to lead one to expect such behavior, the tests were rather far along before the effect became noticeable. This shrinkage would, of course, be dealt with in large-scale operation by carrying out in simple low-pressure equipment the preliminary reduction treatment found most suitable. The catalyst could then be safely transferred to the high-pressure synthesis equipment by taking precautions to avoid contamination or oxidation.

Such a procedure was, in fact, followed in a later series of tests, results of which are reported in Table II. These tests utilized a copper-lined reactor without thermocouple well and with an inside diameter of 0.95 cm. A catalyst of 8 to 30 mesh was used, the other test conditions remaining substantially the same as for the tests reported in the foregoing. The most important change

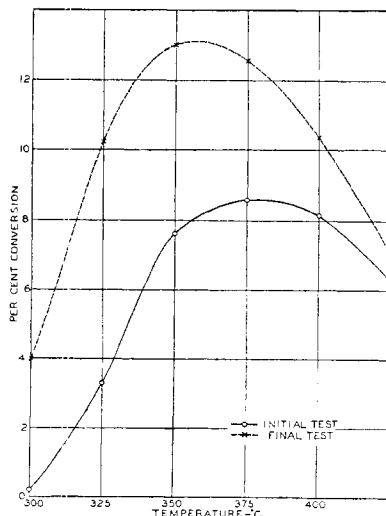


FIGURE 4. METHANOL SYNTHESIS WITH $\text{Zn}_{75}\text{Cr}_{25}$ CATALYST

consisted in reducing the catalysts with the testing gas at 1 atmosphere and at temperatures up to 450° C. before charging into the reactor. Since practically all of the shrinkage had occurred before testing, these data on catalysts high in chromium are more nearly comparable with those on catalysts high in zinc than in the case of the data shown in Figure 3.

TABLE II. VARIATION OF CONVERSION WITH CATALYST COMPOSITION FOR PRESHRUNK CATALYSTS

COMPOSITION	TEMP. ° C. ^a	INLET SPACE VELOCITY	PER CENT CONVERSION
Zn ₉₃ Cr ₇	320	25,000	24.4
Zn ₉₃ Cr ₇	340	25,000	25.2
Zn ₉₃ Cr ₇	340	30,000	26.4
Zn ₉₃ Cr ₇	300	33,000	26.9
Zn ₉₃ Cr ₇	300	25,000	21.8
Zn ₉₃ Cr ₇	320	25,000	17.8
Zn ₉₃ Cr ₇	340	25,000	7.4

^a Temperature at which maximum conversion occurred.

These results, which are much more nearly comparable as to space velocity than those of Figure 3 or Table I, again indicate the superior activity of catalysts having an atomic ratio of zinc to chromium of about 1. The results are also of very nearly the same order as those in Table I, when allowance is made for the different space velocities. This can be done by assuming a similarity in behavior to a Zn₉₃Cr₇ catalyst which gave at 400° C. and 178 atmospheres absolute pressure the results in Table III. [While the data at the higher space velocities are not used here, they are included in Table III because of the scarcity of such published information, despite its importance for commercial design purposes. The only other methanol synthesis tests in which space velocity was the only variable and an extensive range was covered are those reported by Storch (26) who went to 25,000 space velocity. His conversions decrease somewhat more rapidly with increasing space velocity than those in Table III.]

TABLE III. VARIATION OF CONVERSION WITH SPACE VELOCITY

INLET SPACE VELOCITY	PER CENT CONVERSION	INLET SPACE VELOCITY	PER CENT CONVERSION
4,700	18.0	92,000	7.7
18,900	14.1	101,500	7.2
45,700	9.5	190,000	4.9

By graphical interpolation these data in Table III give conversions of 12.4 per cent at 25,000 space velocity and 9.2 per cent at 53,000. Assuming that the same ratio holds for the Zn₉₃Cr₇ catalyst which gave 16.2 per cent conversion at 350° C. and at a space velocity of 53,000 as based on the 4.7 cc. volume of catalyst discharged, the conversion at 25,000 space velocity becomes about 22 per cent. Similarly the maximum conversion obtained with the Zn₉₃Cr₇ catalyst, which, as previously mentioned, was 15.3 per cent at 350° C., was at an actual space velocity of 64,000 as based on the 4.0 cc. of catalyst discharged. Estimating from Table III a conversion of 8.6 per cent at 64,000 space velocity and multiplying the 15.3 per cent by the ratio of 12.4 to 8.6 gives an estimated conversion of about 22 per cent at 25,000 space velocity. Both of these points show a gratifying agreement with the approximately 25 and 21 per cent, respectively, given in Table II, in view of the fact that different reactors and different sizes of catalyst particles were used in the two sets of tests. This agreement also indicates that the data on space velocity *vs.* conversion given in Table III can be safely applied to other catalysts of the same type but of quite different composition.

RESISTANCE TO HIGH TEMPERATURE. The stability shown by these active catalysts was further investigated in a test of another Zn₉₃Cr₇ catalyst. In this test the catalyst was

given a 7-hour preliminary reduction with hydrogen up to 450° C. before being charged into the reactor. The initial test at 300° C. and 33,000 space velocity gave a conversion of 25.2 per cent. A 5-hour treatment with the testing gas mixture at 1 atmosphere and 500° C. did not lower the activity of the catalyst at 300° C., nor did a further 6-hour treatment at 550° C. Five hours more at 600° C. caused a decrease to 20.8 per cent conversion and, after 4 additional hours at 685°, to 8.1 per cent. The catalyst was still fairly active in spite of exposure for 20 hours at temperatures 200° to almost 400° C. above its normal operating temperature, and gave a 15.5 per cent conversion at 340° C.

ACTIVITY OF PURE OXIDES. The number of variables involved in the preparation and testing of methanol catalysts is very large, as has been previously mentioned, and the effects of these variables are in general only approximately known. Comparisons of the data of different investigators tends, therefore, to give only qualitative information, and consideration at this point will be limited to work done at a set of conditions similar to those used by the present authors—i. e., 178 atmospheres absolute pressure, an inlet gas consisting substantially of 1 part of carbon monoxide to 2 parts of hydrogen, and, in most cases, an inlet space velocity of 25,000. Without going into detail, the following conclusions may be drawn after making allowances for the differences in testing conditions. The pure zinc oxide giving the conversions shown in Figure 3 is several times as active as that tested by Morgan, Taylor, and Hedley (17), slightly more active than those of Brown and Galloway (6) and Frolich and co-workers (8, 10), and somewhat less active than that of Lazier and Vaughen (15).

The variety of methods used in preparing the zinc oxide catalysts already mentioned suggested a comparison of catalysts made and tested under identical conditions, except for a single variable. The results of these tests, in which zinc oxide was precipitated from the nitrate by two different precipitating agents are given in Table IV. These show that the zinc oxide precipitated by sodium carbonate is markedly more active than that precipitated by ammonium hydroxide, in agreement with the observations of methanol decomposition activity by Ipat'ev and Dolgov (18) and by Plotnikov and Ivanov (22). The exceptional activity of catalyst 62, which was confirmed in a test of a second sample of the same catalyst, may possibly be due to the fact that a slight insufficiency of sodium carbonate was used, whereas a slight excess was used in the preparation of catalysts 34 and 81.

TABLE IV. EFFECT OF PRECIPITATING AGENT ON ACTIVITY OF ZINC OXIDE CATALYSTS

(At 385° C. and 178 atmospheres)			
CATALYST NO.	PRECIPITATED BY:	INLET SPACE VELOCITY	PER CENT CONVERSION
32	NH ₄ OH	92,000	3.0
36	NH ₄ OH	95,700	2.6
34	Na ₂ CO ₃	94,500	4.7
62	Na ₂ CO ₃	95,000	8.5
81	Na ₂ CO ₃	95,000	5.5

Published data on pure chromium oxide catalysts are somewhat limited, but the results given in Figure 3 and Table I indicate that this catalyst, prepared by precipitation from the nitrate by ammonia, is about three times as active as a methanol catalyst at the same space velocity as the best one made by ignition of the oxalate, as reported by Lazier and Vaughen (15). It was also about twice as active as a gel made by them by precipitation from chrome alum with sodium hydroxide. The tests of pure zinc oxide and pure chromium oxide, made under comparable conditions by Audibert and Raineau (2), showed that the latter had less than one-third the methanol synthesis activity of the former. This result was not confirmed in the present work, which revealed that the

zinc oxide has less activity than the chromium oxide, both oxides being precipitated by ammonia, when allowance is made for the shrinkage in volume of the latter during testing. This adjustment for space velocity, using the data in Table III as before, raises the maximum observed conversion by chromium oxide from 6.8 per cent at 56,000 space velocity to an estimated conversion of 9.3 per cent at 25,000 space velocity. This can be compared with the maximum observed conversion by zinc oxide of 6.0 per cent at 25,000 space velocity. The chromium oxide gave at 375° C. a product containing 96 per cent methanol, while that of zinc oxide at the same temperature contained 86 per cent methanol. At 400° C., the temperature of maximum activity for both catalysts, the products contained 91 and 78 per cent methanol, respectively. The superiority of the chromium oxide as regards injury at high temperature and breakage due to handling and testing was also marked.

ACTIVITY OF MIXTURES. Among those who have tested mixtures of zinc and chromium there are several who have employed testing conditions quite similar to those used in the present work. Morgan, Taylor, and Hedley (17) obtained about 9 per cent conversion at 200 atmospheres, temperature not reported but presumably the optimum, 33,000 space velocity, ratio of hydrogen to carbon monoxide of 2, with a 75 atomic per cent zinc catalyst prepared by adding chromium trioxide to zinc oxide. A catalyst containing 50 atomic per cent zinc, the method of preparation of which was not described, gave the same conversion.

The maximum conversion obtained by the authors with a $Zn_{75}Cr_{25}$ catalyst was 14.0 per cent at a space velocity of 42,000 as based on 5.9 cc. of catalyst discharged. Adjustment of this to 33,000 space velocity, but neglecting the effect of the higher pressure used by Morgan, Taylor, and Hedley, gives an estimated conversion of 17 per cent as against their 9 per cent. A rough comparison with their $Zn_{50}Cr_{50}$ catalyst can be made by interpolation between the data in Table II for the $Zn_{53}Cr_{47}$ and the $Zn_{38}Cr_{62}$ catalysts. A conversion of about 26 per cent could presumably be expected for a $Zn_{50}Cr_{50}$ catalyst, indicating that the catalysts described in the present work, prepared from trivalent chromium, were two to three times as active as those of the above-mentioned investigators in which the chromium was initially in the hexavalent form. Further evidence on this point is found in the paper of Brown and Galloway (5), who tested a 50 atomic per cent zinc catalyst made from zinc oxide and chromium trioxide by the method of Gröger (11) and obtained 9.6 per cent conversion at 180 atmospheres, 400° C., 16,200 space velocity, and hydrogen-carbon monoxide ratio of 2. A basic chromate (assumed after reduction to be $2ZnO \cdot \frac{1}{2}Cr_2O_3$, equivalent to about $Zn_{66}Cr_{34}$) made by adding zinc nitrate to a solution of sodium chromate, gave 7.4 per cent conversion when tested as above. Adjustment of the data of Table I to the same conditions of space velocity and catalyst composition by the method used above again indicates that conversions between two and three times those obtained by Brown and Galloway might be expected from catalysts prepared by the method used by the authors.

Two methods were used in the preparation of the series of mixed oxide catalysts tested by Cryder and Frolich (8). Catalysts containing more than 50 atomic per cent zinc were made by evaporating to dryness mixtures of zinc hydroxide, precipitated from the nitrate by ammonia, and chromium trioxide. Those containing less than 50 atomic per cent zinc were made by mixing equivalent amounts of zinc hydroxide and chromium trioxide, adding this to a calculated amount of chromium nitrate solution, and precipitating. The tests were carried out at 204 atmospheres, 350° C., hydrogen-carbon monoxide ratio of 2.5, using equal weights of catalysts. The space velocity, as based on the volume of catalyst used,

was not given; however, assuming that the catalysts weighed on the average 1 gram per cubic centimeter gives inlet space velocities of about 30,000 when no conversion takes place and about 33,000 at the maximum conversion observed. The results are, therefore, roughly comparable to those in the present work, and it is found in most cases that the Cryder and Frolich catalysts have about half the activity shown in Figure 3 and Table I.

To add to the meager evidence as to the relative merits of the two types of chromium compounds as starting materials, three catalysts containing 50 atomic per cent each of zinc and chromium were prepared and tested. Two of these were made by evaporating to dryness a mixture of ordinary dry-process zinc oxide and chromium trioxide. These catalysts were found to give 12.5 per cent conversion. The third catalyst was prepared as a definite compound by the method of Gröger (11), and gave only 9 per cent conversion. As catalysts made by ammonia precipitation from the nitrates gave 25 per cent conversion under the same conditions, the superiority of the latter method of preparation seems well established.

The low activity of the 92 atomic per cent chromium catalyst (Figure 3 and Table I), as compared with the pure chromium oxide, was confirmed in the tests of methanol decomposition activity of the same series of catalysts by Huffman and Dodge (12). Their tests of catalysts containing 85, 90, and 97 atomic per cent chromium showed that these also possessed a lower decomposition activity than pure chromium oxide, the relative activities being such as to verify the shape of the curves in Figure 3. It appears therefore that the addition of zinc oxide up to about 25 atomic per cent lowers the synthesis activity of a chromium oxide catalyst.

GLOW PHENOMENON. The catalyst containing 92 atomic per cent chromium is of particular interest in that it alone displayed the familiar "glow phenomenon" during the synthesis tests. Early in the first test of this catalyst, while raising the temperature from 325° to 350° C., a spontaneous rise in temperature to 440° C. was observed. The catalyst then cooled to 350° C., the whole phenomenon requiring about 5 minutes. Again, in going from 400° to 425° C., a maximum of 500° C. was attained. In testing a second sample the standard 1-atmosphere preliminary procedure was modified so that a temperature of 450° C. was finally reached. During normal high pressure operation a maximum of 440° C. occurred between the 350° and the 375° C. runs, and another of 475° C. between the 425° and 450° C. runs. A third sample of the catalyst was then given a preliminary procedure concluding with periods at 450° C. and 1, 30, and 100 atmospheres. During testing, this catalyst attained a temperature of 465° C. between the 375° and the 400° C. runs. It was evident that the higher temperatures in the preliminary treatment delayed the occurrence of the heat effect. No doubt the relatively great heat capacity of the reactor kept the maximum temperatures low, and the effect is an indication of the frequently observed glow phenomenon. Analyses of the samples of product formed during such periods were hardly accurate enough to indicate water formed either by dehydration or reduction of the catalyst. According to Lazier and Vaughn (15), however, water is given off but no reduction that can be observed takes place when the glow phenomenon occurs with hydrated chromium oxides. In all three tests of the 92 atomic per cent chromium catalyst, it was found that the material had undergone a 60 per cent decrease in volume and a 45 per cent decrease in weight. No similar heat effect was observed in testing any other catalysts, and the procedure was such that the phenomenon would not ordinarily have escaped notice. From previously published work on chromium oxide it appears likely that it also occurred in the case of the pure chromium oxide catalyst. The test

of this catalyst happened to come at a time when attention to details of control might have prevented observation of the phenomenon.

PURITY OF PRODUCT. The liquid product synthesized by the catalysts was substantially pure methanol with a small percentage of water. In only one case was there an indication of the presence of other materials, probably higher alcohols. Distillation tests of the products of all catalysts except the pure zinc oxide and that containing 92 atomic per cent chromium showed maximum methanol percentages between 96.4 and 99.8 per cent by volume. The two catalysts just referred to gave maxima of 86 and 79 per cent methanol by volume, respectively. In all cases the percentage of methanol decreased with increasing catalyst operating temperature. The following results with $Zn_{85}Cr_{15}$ are an example: 99.8 at 300° C., 97.9 at 325°, 96.6 at 350°, 94.1 at 375°, 94.1 at 375°, 93.7 at 400°, and 90.0 at 425°. As previously mentioned, the difference between the methanol content as calculated from specific gravity measurement and as determined by distillation increased with decreasing catalyst activity and with increasing catalyst temperature. As the higher methanol content was shown by the specific gravity measurement, it is possible that the difference was due to the presence of dimethyl ether in the product. The experiments carried out by Brown and Galloway (5) with normal zinc chromate under conditions similar except as to space velocity to those used by the authors showed that almost one-fourth as much of the reacting carbon monoxide was converted to dimethyl ether as to methanol at 397° C. and 3000 space velocity. This fraction decreased with increasing space velocity, but it is conceivable that even at 25,000 space velocity dimethyl ether formation would partially account for the discrepancy in the analysis and for the water in the product. No other explanations are available, as this phase of the work was not further investigated.

SUMMARY

Mixtures of zinc and chromium oxides, made by precipitation from a solution of the mixed nitrates by ammonia, are found to be active and physically rugged methanol catalysts. Short-time tests indicate that the most active mixture has approximately the composition $Zn_{75}Cr_{25}$. This is in agreement with the reports of other investigators and with the generally held opinion that an excess of zinc is necessary. But the catalysts of higher chromium content than this are found to increase in activity during extended testing, this improvement being accelerated by operation at temperatures up to 100° C. above the temperature of maximum activity. This behavior, which had not been reported in previously published work, located the composition of maximum activity in the region of $Zn_{50}Cr_{50}$. This catalyst produces very nearly pure methanol, appears to be uninjured by long use or by operation at temperatures considerably above the normal operating temperature, and shows good physical ruggedness. It is probable that the most active mixture would contain an excess of chromium oxide since it is found that chromium oxide is in all respects superior to a comparable zinc oxide as a methanol catalyst.

It is found by methanol synthesis tests and confirmed by previously reported methanol decomposition tests that addition of up to 25 atomic per cent zinc oxide to chromium oxide gives a catalyst of lower activity than chromium oxide alone.

Precipitation of zinc oxide by sodium carbonate was found to give a more active catalyst than when ammonia was used as the precipitating agent. The most active zinc oxide catalyst was made by using a slight insufficiency of sodium carbonate.

Catalysts prepared by several methods which use chromic acid as the source of chromium are much less active than those in which the chromium is initially in the trivalent form.

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